EARTH'S OXYGEN AND PHOSPHORUS CYCLES AND THE EVOLUTION OF ANIMAL LIFE

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EARTH'S OXYGEN AND PHOSPHORUS CYCLES AND THE EVOLUTION OF ANIMAL LIFE

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SYMBOLS AND ABBREVIATIONS

cGENIE	Grid ENabled Integrated Earth system
O_2	oxygen
CO_2	carbon dioxide
Cr	chromium
pO_2	partial pressure of oxygen
PAL	present atmospheric level
POL	present oceanic level

ABSTRACT

The purpose of this study is to reconstruct an environmental context for the emergence and expansion of early animal life during the Middle Proterozoic (~1.8–0.8 billion years ago). Specifically, we examined the spatially and temporally evolving Earth surface ocean oxygen (O_2) concentration impacted by atmospheric partial pressure of oxygen (pO_2) and phosphorus levels. We exploited a quantitative biogeochemical model - the Grid ENabled Integrated Earth system (cGENIE) model, which consists of a reduced physics 3-D ocean circulation model coupled to a 2-D energy-moisture balance model of the atmosphere and a dynamic-thermodynamic sea-ice model. Our results suggest a challenging evolutionary landscape for basal metazoan life characterized by spatiotemporal variation in surface ocean oxygen level and prevalent benthic anoxia even with surface ocean-atmosphere oxygen level sufficient to support basal biological activities. By studying the environmental variability presented during the evolutionary history of complex life on Earth, we are thus equipped with a valuable tool to examine the potential biotic complexity throughout the universe.

CHAPTER 1

INTRODUCTION

Atmosphere-ocean oxygen levels are believed to have constrained the evolution of complex life on Earth. For example, "O_2 is the only respiratory electron acceptor that can meet the metabolic demands required for attaining the large sizes and active lifestyles characteristic of metazoan life" (Reinhard et al., 2016). Specifically, the emergence of different stages of early complex life may have depended on surpassing "threshold" oxygen levels.

Most previous work studying the relationship between early life evolution and Earth's oxygen levels has been either "biological" or "geochemical". Experimental work with the modern demosponge Halichondria panacea suggests that early animals could respire at very low oxygen levels ($\sim$1–10 $\mu mol \cdot kg^{-1}$ for air-saturated water at 25 °C and a salinity of 35‰). At the same time, geochemical estimates of atmospheric pO_2 levels span from values well below toleration level of aerobic organisms on long timescales to values well above requirement for animal respiration. Although it is reasonable to infer a "respiratory barrier" to emergence and expansion of early animals, this approach has several drawbacks such as the neglect of spatial heterogeneity in oceanic O_2 levels.

In a study which explored a biogeochemical model approach and thus provided a new framework for understanding the subject studied, "Earth's oxygen cycle and the evolution of animal life" (Reinhard et al., 2016), which inspired this thesis research, Reinhard and fellow researchers found large spatiotemporal variations in surface ocean O_2 levels and prevalent benthic anoxia in a world with much lower atmospheric pO_2 than that at

present, which would have led to long-term ecological inhibition of animal life on Earth for much of Middle Proterozoic time. However, by keeping CO_2 and nutrient values at or close to modern level, Reinhard's research on surface ocean O_2 levels could be significantly improved in accuracy by approximating pCO_2 and nutrient parameters regarding Mesoproterozoic conditions.

This study is designed to achieve this improvement. We first designated a Mesoproterozoic pCO_2 value and selected appropriate ranges of pO_2 and oceanic nutrient values based on related research. Since phosphorus is typically considered to be the ultimate nutrient which limits productivity on a geological timescale (Planavsky et al., 2015), we focused on phosphate as the nutrient tracer in our model. We then used the cGENIE model to evaluate the spatial and temporal variability in surface ocean oxygen levels on Earth prior to the emergence of complex life, in order to propose a conceptual model that links Earth's oxygen cycle and early evolution of animal life.

CHAPTER 2

LITERATURE REVIEW

The long-term evolution of ocean-atmosphere oxygen levels has been prevailingly considered to be linked at a basic level to the evolution of complex life on Earth. Molecular O_2 is a crucial component for synthesis of regulatory membrane lipids and structural proteins in eukaryotic organisms. O_2 is also considered to be the most energetic of terminal oxidants used in biological metabolism. How planetary redox evolution controlled the emergence and expansion of metazoan life has been the subject of intense discussion, which focused on threshold levels of environmental free O_2 that early evolving life needed to survive under constrained conditions. However, it is not straightforward to define such thresholds, as O_2 levels need to be distinguished for the emergence and diversification of different organisms in distinct time periods. While some of organisms may require a discrete threshold, the others may live with O_2 levels depending strongly on environmental variability.

Most existing literature on the co-evolution of metazoan life and surface O_2 levels are either constraining threshold environmental O_2 levels for different organisms, or constraining environmental O_2 levels before, during, and after the emergence of metazoan life. While some simulations indicate that local biological O_2 production may satisfy respiratory needs of organisms regardless of background atmospheric pO_2, other experimental work and theoretical calculations suggest that oxygenation of Earth's surface plays an important role in early animal evolution. While focusing on the Middle to Late Proterozoic, Reinhard et al (2016) applied a series of quantitative biogeochemical

models and found that large spatiotemporal variations in surface ocean O_2 levels and pervasive benthic anoxia were expected in a world with much lower atmospheric pO_2 than at present (Reinhard et al., 2016).

Although the current discussion on the relationship between surface oxygen levels and the evolution of early metazoan life shows a relatively sharp dichotomy, that either environmental oxygen levels has been of primary importance for the rise of animal life, or has not at all. Establishing the validity of either hypothesis would significantly push forward the efforts to understand the role environmental factors play in early life evolution.

Taking an isotope-analysis approach, Planavsky et al. (2014) interpreted chromium (Cr) isotope data from a suite of Proterozoic sediments from over the world from similar depositional environments from Phanerozoic period, and found evidence for inhibited oxidation of Cr at Earth's surface in the mid-Proterozoic (Planavsky et al., 2014). These results suggested a temporal overlap, which occurred between ~0.8 and 0.7 Ga, between the emergence of stable environments favorable for animal evolution and the divergence of basal metazoan clades, and thus concluded that Earth's oxygen cycle is a crucial factor forming the evolutionary landscape in the late Proterozoic.

The study of Ozaki and Tajika (2013) provides a holistic view on the surface O_2 activity during the time of early life emergence. Factors such as the pO_2, the continental shelf area, and the riverine input rate of reactive phosphorus to the oceans were examined through sensitivity experiments to gain insight into the mechanisms of variations in oceanic chemical dynamics (Ozaki and Tajika, 2013). Ozaki and Tajika (2013) employed an oceanic advection-diffusion-reaction biogeochemical cycle model to accomplish this

goal. The result that widespread oceanic anoxia and euxinia took place when pO_2<0.145 and <0.125 atm respectively agrees with the low O_2 levels in the mid-Proterozoic (<0.1% PAL) and thus harsh respiratory environment for metazoan evolution found by Planavsky et al (2014).

However, Mills et al. (2014) challenged the idea that environmental O_2 levels are closely bonded with early life evolution by providing experimental evidence suggesting that the last common ancestor of animals could have thrived in oxygen levels as low as 0.5% to 4% PAL, which were likely met on Earth well before animals evolved (Mills et al., 2014). In addition, all major eukaryotic lineages contain genes and enzymes allowing for facultatively anaerobic energy metabolism (Reinhard et.al, 2016), thus it is possible that early animals were able to respire at very low environmental O_2 levels and periodic episodes of local anoxia probably would not have been so much a problem. Adding to the complication, a range of biogeochemical models applied to simulate the disequilibrium between surface marine and atmospheric oxygen levels indicate that local biological O_2 production in some regions of the surface ocean may have been enough to sustain the respiratory requirements of basal metazoan organisms regardless of background atmospheric pO_2 (Kasting, 1991).

In order to evaluate the significance of an environmental O_2 threshold to animal emergence and expansion during a given period in Earth's history, theoretically one could compare a geochemical estimate of atmospheric pO_2 to an estimate of the oceanic O_2 level required for respiration in a particular metazoan organism. However, the drawbacks of this approach exist in the neglection of spatial heterogeneity in oceanic O_2 levels and the possible significant oscillation of O_2 levels whose average value over a

long period appears to be favorable for animal life. It also ignores the variable O_2 demand during an organism's life span and the interactions between O_2 and other key environmental factors.

CHAPTER 3

METHOD AND MATERIAL

In order to evaluate the impact on early metazoan emergence and evolution posed by the oxygenic environment of Mesoproterozoic Earth, we employed a 3-D Earth system model to examine the spatial variability in surface ocean oxygen and the surface-benthic O_2 relationship at a range of atmospheric pO_2 values of Middle to Late Proterozoic Earth.

The atmospheric pO_2 levels of 0.1%, 1% and 5% PAL were chosen in order to achieve comprehensive estimates for the time period studied. While Cr isotope results suggest <0.1% PAL oxygen, geochemical study of redox-sensitive trace metals indicates a range of 3.8%-6.2% PAL oxygen, with 1.3% an unlikely but possible minimum (Zhang et al., 2016). We quantitatively reconstructed marine nutrient inventory by reducing the initial oceanic phosphorus inventory in our sensitivity simulations to 1%, 10% and 100% of the modern value to account for the hiatus in phosphorite deposition during Mesoproterozoic (Derry, 2015). We also assumed many parameters, some of which were modern boundary conditions, such as continental configuration (e.g., large-scale ocean circulation), while the others were obtained from related researches on Middle to Late Proterozoic Earth, such as climate, e.g., pCO_2 = 10PAL as inferred from calcified cyanobacteria (Kah et al., 2007).

The cGENIE model is a reduced physics 3-D ocean circulation model coupled to a 2-D energy-moisture balance model of the atmosphere and a dynamic-thermodynamic sea-ice model. It is run on a remote cluster using commonly available command-line software programs (e.g., Terminal). It is calibrated by assimilating observed marine geochemical

data and the ensemble Kalman filter methodology. The ocean circulation model advects, diffuses and convects the oceanic concentrations of biogeochemical tracers, such as total dissolved inorganic carbon, alkalinity, phosphate and oxygen, online along with temperature and salinity (Ridgwell et al., 2007).

BIOGEM/the 3D marine biogeochemistry module, which is the focus of our research, is developed to calculate the redistribution of tracer concentrations happening through the removal from solution of nutrients by biological activity in surface ocean. The constituent elements in the organic product of this process are later turned into inorganic solution by decomposition and dissolution in a greater depth. Further redistribution of tracers happens through processes such as gas exchange with the atmosphere.

The model has been used successfully to interrogate some older intervals in Earth's history, such as the Cretaceous, the end-Permian, and the Archean/Proterozoic. Overall, the Earth system model is able to simulate a wide variety of dissolved and isotopic species relevant to the study of modern global biogeochemical cycles and past global environmental changes.

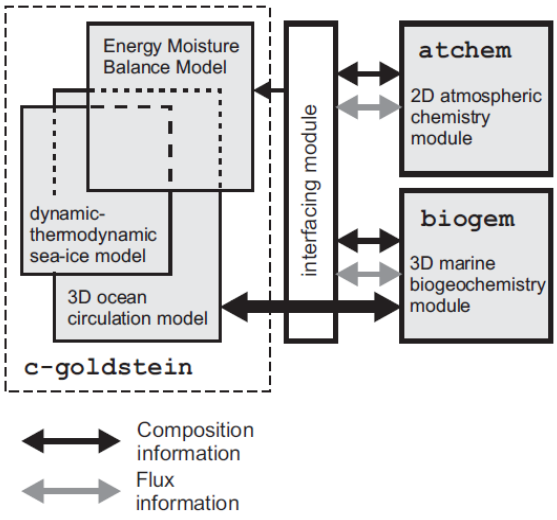


Fig.1 Schematic of the relationship between different model components of cGENIE

For the actual modelling process, we first set up “base configurations” to use in all of our simulations, which involve picking the chemical tracers we wanted the model to track, setting the solar output, and establishing whether we wanted various tracers to remain constant or respond dynamically to our experiments. Then, we designed “user configurations” for pCO_2, phosphorus, and pO_2. Overall, we did nine simulations covering all of the various combinations of said parameter values.

pO_2 (PAL) / $[PO_4^{3-}]$ (POL)	0.1%	1%	5%
1%	0.1%×1%	1%×1%	5%×1%
10%	0.1%×10%	1%×10%	5%×10%
100%	0.1%×100%	1%×100%	5%×100%

Table.1 Combinations of input parameters designed for experiments

For each of the simulations, we first span the model up for 10,000 years so that all tracers came to a steady state, then we took those steady state spin ups and ran 10-year experiments in which we recorded output monthly to explore seasonal changes in surface (and deep ocean) O_2 concentrations.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Spatiotemperal oxygen variability in surface ocean

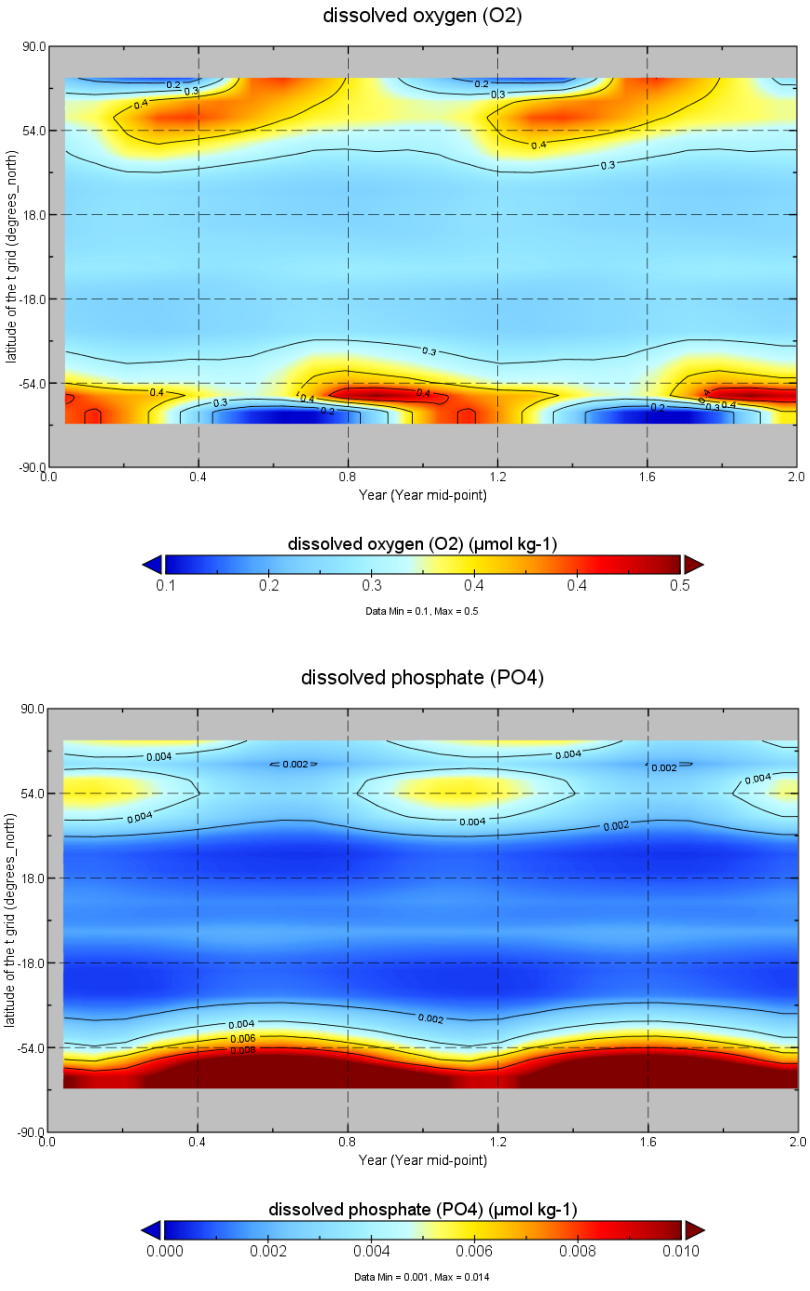
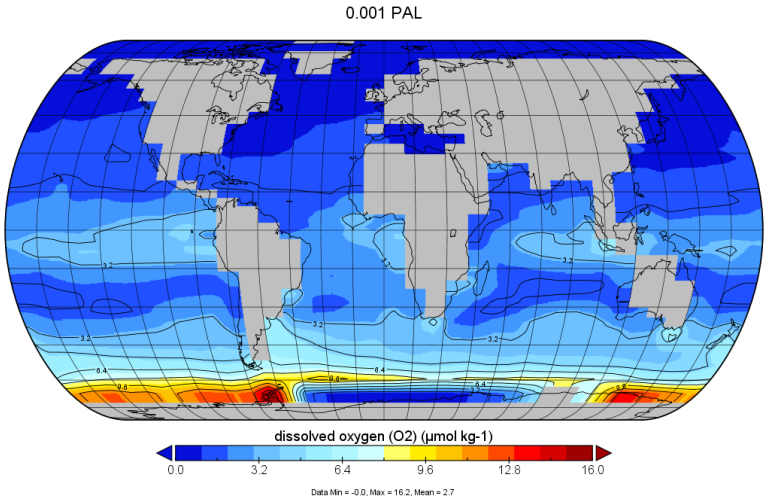


Fig.2 Seasonal variability of surface ocean dissolved oxygen and phosphate (0.001PAL O_2+0.01POL PO_4)

The first plot presents an example of latitudinal variation in surface ocean oxygen concentration with time in our model. Generally, the highest accumulated concentration in middle to high northern latitudes occurs between spring and summer, and the lowest occurs between fall and winter. This trend can be explained by the fact that oxygen solubility in ocean is higher when the atmospheric temperature is lower, and vice versa. This is also why the ocean concentration in the two hemispheres shows opposite trend in seasonal variability.

The second plot presents an example of latitudinal variation in surface ocean phosphate concentration with time in our model. Compared to the aggregation of nutrient in middle to high southern latitudes ocean, the tropical and subtropical surface ocean appear to be consistently deprived of dissolved phosphate. This observation, combined with the consistently low or moderate oxygen concentration in the conventionally productive regions of surface ocean and the drastic seasonal variability of oxygen concentrations in high-latitude regions of surface ocean, indicates a challenging evolutionary landscape for aerobic metazoan organisms.



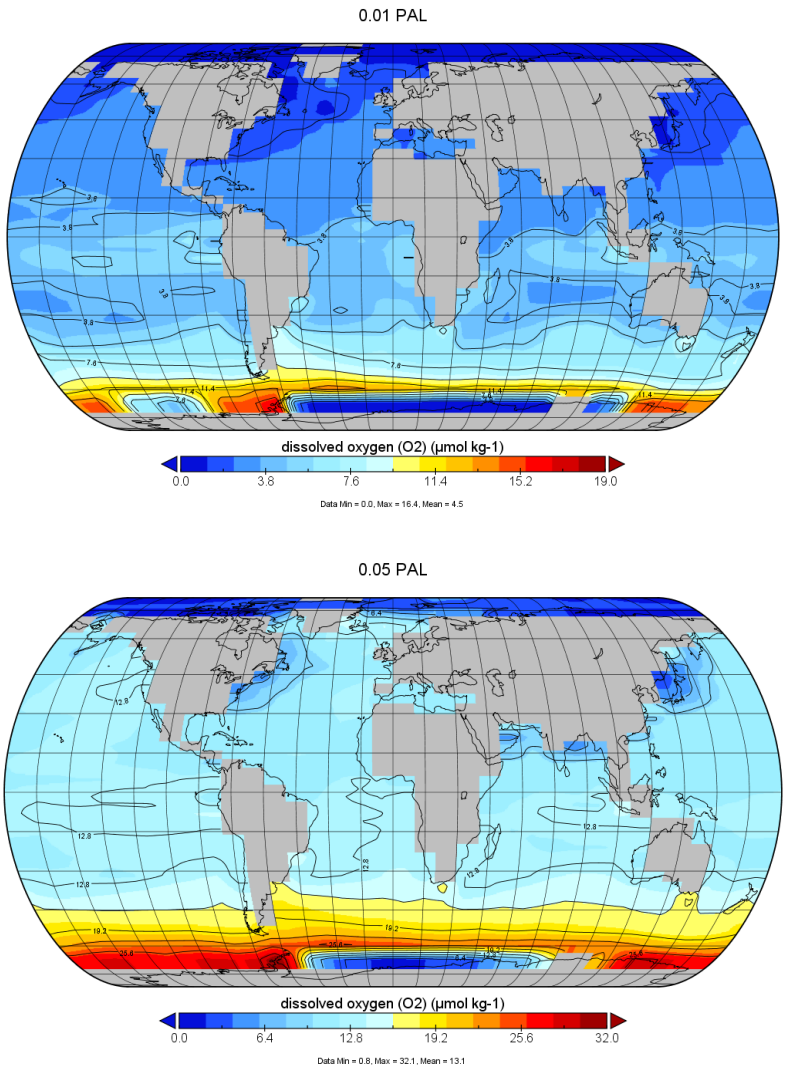


Fig.3 Surface ocean dissolved O_2 distribution at different atmospheric pO_2 levels and 1POL PO_4

The three maps demonstrate the spatial variation in dissolved oxygen concentrations in surface layer of the ocean with different level of atmospheric pO_2. At the same nutrient level and time period, the surface ocean around the globe becomes more oxygenated as the atmospheric oxygen level increases. However, the tropical and subtropical regions still appear to have less dissolve oxygen than the colder, high latitude surface ocean for all three distributions. This stands out as a significant inconsistency with previous work which shows a critical transition at pO_2 levels around 2.5% PAL, below which point surface ocean oxygen distributions are controlled by the biological activity in surface

ocean rather than the atmosphere (Reinhard et al., 2016). In our model, when atmospheric pCO_2 was set to 10PAL according to estimate of Mesoproterozoic level, most of the surface ocean is near gas exchange equilibrium with atmospheric pO_2 for the whole range of atmospheric pO_2 level. This discrepancy might be explained by the difference in ocean circulation setting between the Earth system model employed. The patterns of large-scale ocean circulation under different continental distribution and their relationship with early metazoan life could be the focus of future research.

4.2. Decoupling between atmosphere-surface ocean O_2 dynamics and benthic ocean O_2 level

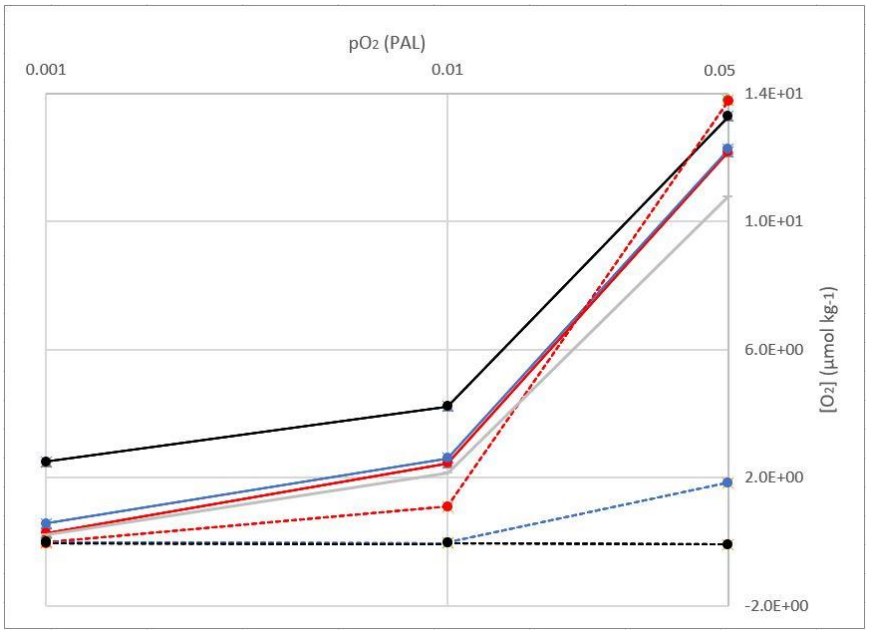


Fig.4 Maximum dissolved oxygen concentration in the surface ocean (solid line) and the benthic ocean (dashed line) as a function of background atmospheric pO_2 value at three [PO_4^{3-}] levels of 0.01POL(red), 0.1POL(blue), 1POL(black). Grey solid line represents the estimated surface ocean [O_2] with gas exchange coefficient for air-saturated water at 24 °C and a salinity of 35‰.

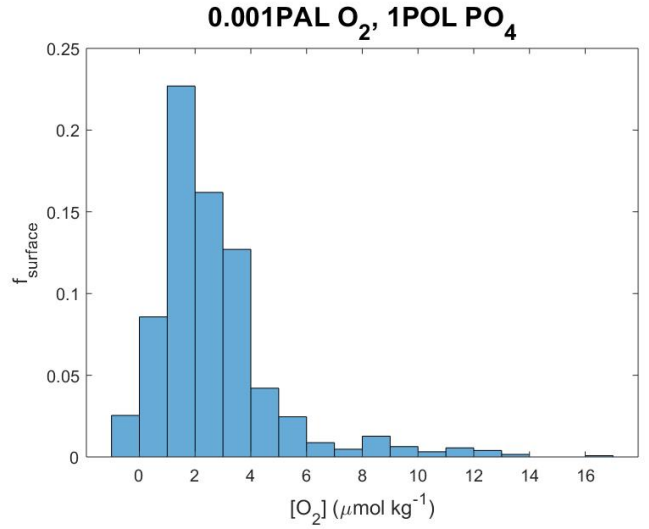
To roughly evaluate the relative importance of atmospheric pO_2 and oceanic phosphorus level as factors acting on surface and benthic ocean oxygen concentrations, we plotted maximum seasonal dissolved oxygen concentration in the surface and benthic ocean as a

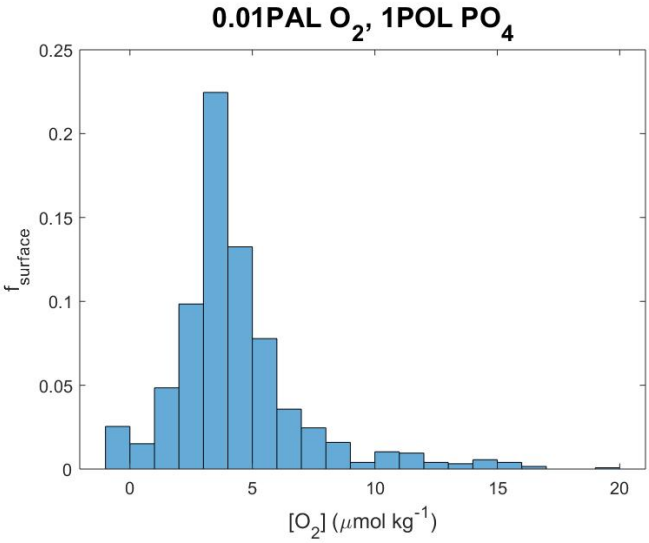
function of background atmospheric pO_2 value at three [$PO4^{3-}$] levels. As shown in the plot, change in surface ocean phosphate level may be correlated with a slightly variation in magnitude of surface ocean oxygen level, but the overall positive relationship between which and atmospheric pO_2 remains unaffected. When it comes to the benthic ocean, however, different surface ocean phosphate levels appear to have a greater impact on oxygen concentration. When the input level is set high enough, i.e. 1POL, the positive trend existed between atmospheric pO_2 and ocean dissolved oxygen level is even altered.

Therefore, it can be inferred from the plot that the variation in atmospheric pO_2 levels has a relatively major impact on surface ocean oxygen concentration, and the surface ocean dissolved phosphate value plays a stronger role acting on benthic ocean oxygen concentration. This conclusion is supported by the simple fact that while organisms living in surface ocean consume nutrients and produce oxygen, they also form organic matters which are oxidized by bacteria while sinking into the deeper layer of ocean. Thus, an increase in surface ocean nutrient level, e.g., phosphate, would lead to a severer and more pervasive benthic ocean anoxia. In addition, the observation that at the lowest phosphorus level (0.01POL) and the highest pO_2 level (0.05PAL), the dissolved oxygen concentration in benthic ocean is close to or even higher than that in surface ocean can be similarly explained by the disappearance of biological activity in a surface ocean almost entirely devoid of nutrient. When gas exchange mechanism is the only factor impacting the amount of dissolved oxygen in surface ocean, as represented by the grey line, its behavior is almost identical with the red solid line as expected.

In sum, this decoupling between atmosphere-surface ocean oxygen dynamics and benthic ocean oxygen availability implies a restriction on the development of basal metazoan life

despite background atmospheric pO_2 level considered to be sufficient for respiration, with the pervasiveness of benthic anoxia depends on nutrient limitation of biological oxygen production in surface ocean during Middle to Late Proterozoic era.





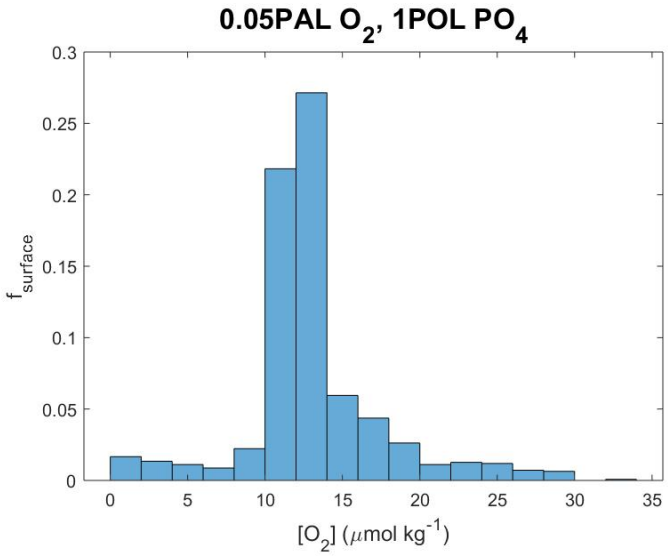
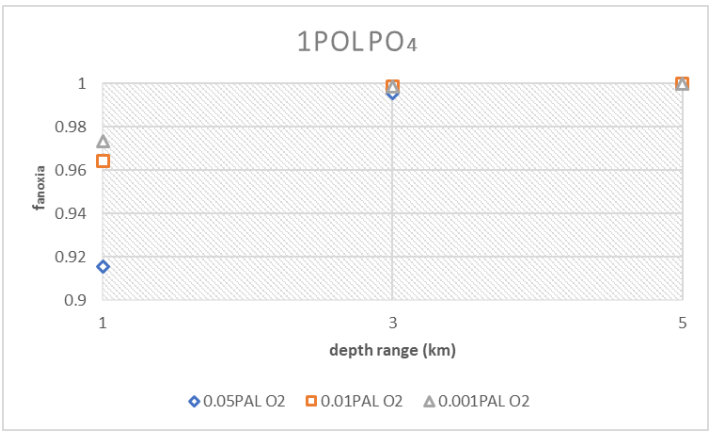
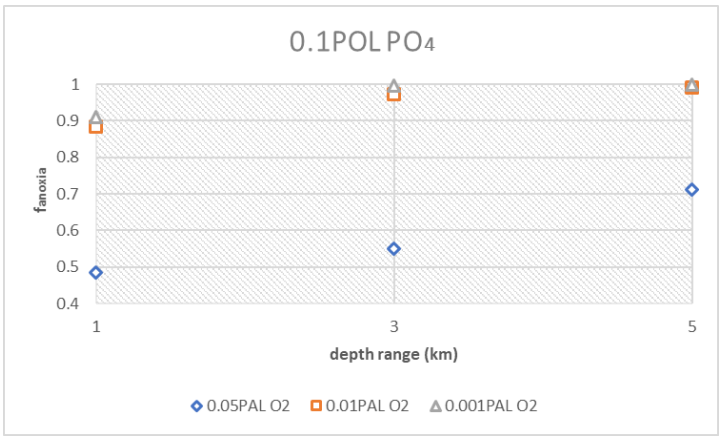


Fig.5 Frequency distributions for dissolved oxygen concentration in surface ocean grid cells





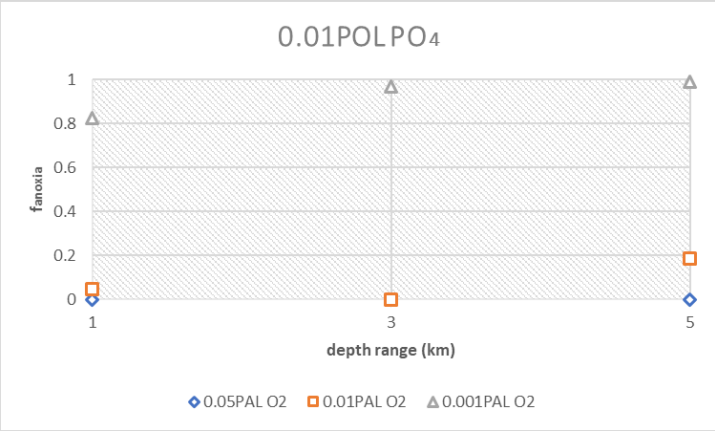


Fig.6 The fraction of benthic grid cells that are anoxic for a range of pO_2 and $[PO_4^{3-}]$ levels

The three plots in Fig.5 present the relative frequency distributions for dissolved oxygen concentration in surface ocean at 1POL phosphate level. When combined with the first plot in Fig.6, which shows the fraction of anoxic benthic grid cells for a range of atmospheric pO_2 levels at the same phosphate level, it is observed that the benthic ocean exhibits a pervasive anoxic environment for the whole range of atmospheric pO_2 level while the corresponding surface ocean has oxygen concentration sufficient for respiration. This comparison further indicates a strong decoupling between surface ocean-atmosphere O_2 dynamics and oxygen availability in benthic ocean, especially at pO_2 levels below 5%PAL.

The other two plots in Fig.6 corroborates our finding in Fig.4 that when the surface ocean dissolved phosphate level is set low enough, it is possible that the difference in oxygen concentration between surface and benthic ocean nearly disappears. Nevertheless, at a phosphate level ten times smaller, as shown in the second plot in Fig.6, the benthic ocean grid cells are still dominated by an anoxic condition no matter what the atmospheric pO_2 level is set to. It is worth pointing out that the upper ocean grid size in our model does not

fully resolve the shallowest of continental margin settings, thus it will be important to investigate the upper ocean in high-resolution models in future research.

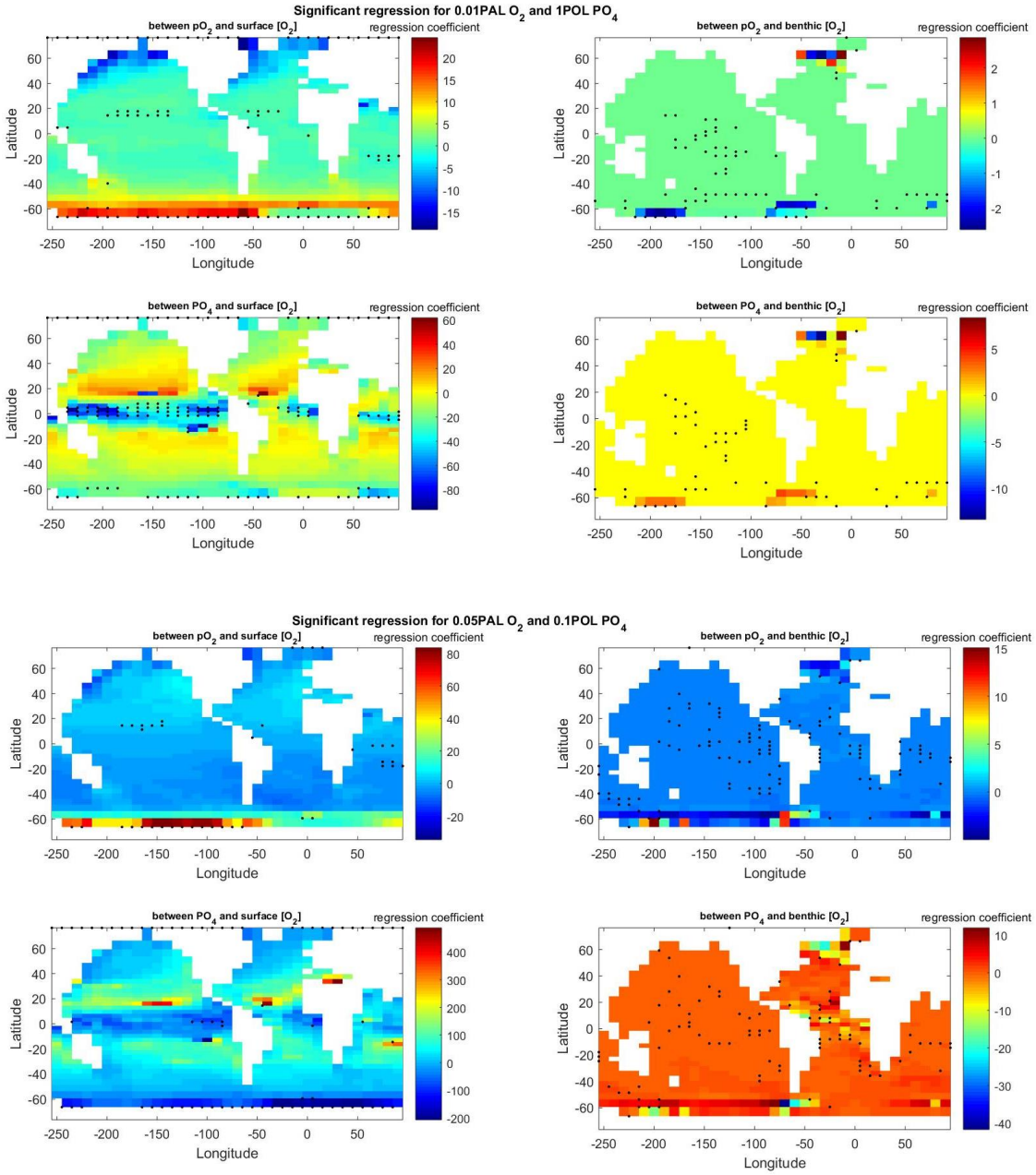


Fig.7 Sample groups of maps of significant regression coefficient between pO_2/dissolved phosphate and surface/benthic(~1km) ocean oxygen concentration.

In order to more closely evaluate the decoupling indicated by previous plots and other potential relationships, we tested the significance of regression between pO_2/dissolved

phosphate and surface/benthic ocean oxygen concentration and plotted nine groups of regression coefficient maps where significant regression is indicted by black dot. For surface ocean, the location of significant trend for both pO_2 and phosphate is generally within tropical regions and high-latitudinal area. For phosphate especially, the significant trend is usually the most negative within the tropical region. Since the significant trend for pO_2 within the same region is only slightly positive, the surface ocean oxygen concentration in the tropics can hardly get too high. It is worth noting here that we tried to keep our atmospheric pO_2 level constant within each experiment by letting the model restore it to initial value automatically after running for a certain period of time. Thus for future research, making atmospheric pO_2 respond dynamically to the experiments may show trends that are more apparent in magnitude and more variable in geography.

For benthic ocean, significant trend can exist anywhere throughout the ocean floor. However, most of the significant regression coefficients for benthic ocean oxygen levels have magnitude close to zero and much smaller than those for surface ocean oxygen levels. Once again, it is shown that the oxygenic condition in benthic ocean during Mesoproterozoic era would be highly variable across different regions and largely isolated from oxygen-associated activities in the surface ocean, and thus creating a challenging evolutionary background for marine organisms with a benthic life stage.

CHAPTER 5

CONCLUSION AND FUTURE WORK

The results obtained from our model characterize the ocean on Earth during Mesoproterozoic era with high spatiotemporal variability in dissolved oxygen level and significant decoupling between surface ocean oxygen dynamics and benthic ocean oxygen availability. While tropical and subtropical regions of the surface ocean are consistently low in oxygen concentration throughout a year, the polar sea water oscillates drastically in oxygen level along with the season. In addition, while increase in atmospheric pO_2 level may cause a rise in the surface ocean oxygen concentration, the negative trend between dissolved phosphate and the latter will weaken the effect of this gas exchange mechanism especially in tropical and polar regions. Altogether, the temporal variation in oxygen availability in polar regions and the interplay between oxygen and nutrient levels in tropical regions imply an unfavorable evolutionary landscape for the formation of complex metazoan life preceding Late Proterozoic on Earth.

Moreover, even when the surface ocean has sufficient oxygen to support respiration, our results indicate a pervasively anoxic ocean floor where the oxygen distribution controlled by atmospheric pO_2 and nutrient level is highly variable throughout the globe. Considering the absence of phosphorite deposition during Mesoproterozoic (Derry, 2015), and that the benthos may be spatially dependent on the organic matter from the water column above as energy source, basal metazoan organisms with a benthic life stage are expected to be hindered severely from large-scale expansion in our model. Later in

time, the Earth ocean might be moved out of this oxygen-limited and nutrient-limited state by tectonic movements which caused increase weathering and phosphorus release (Planavsky, 2015). Also in light of Late Proterozoic atmospheric oxygen enrichment, the said spatiotemporal fluctuation in environmental oxygen level might have driven organisms to diversify genetically and expand geographically.

Future research could focus on the patterns of large-scale ocean circulation under different continental distribution and their relationship with early metazoan life. It will also be important to investigate the upper ocean in high-resolution models. Lastly, making atmospheric pO_2 respond dynamically to the experiments may be able to tell more variable and accurate information about the relationship between pO_2 and ocean oxygen concentration.

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APPENDIX

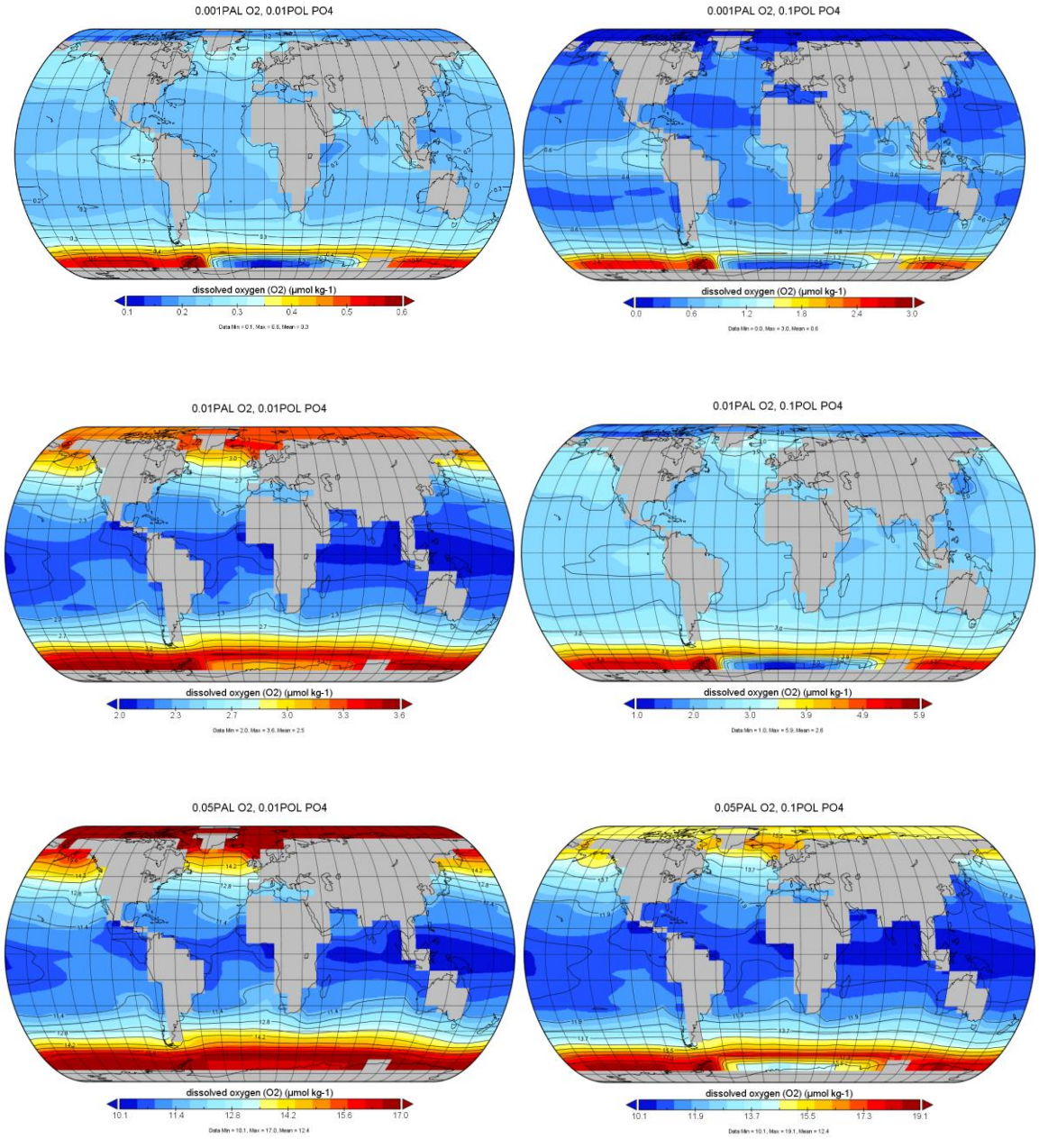
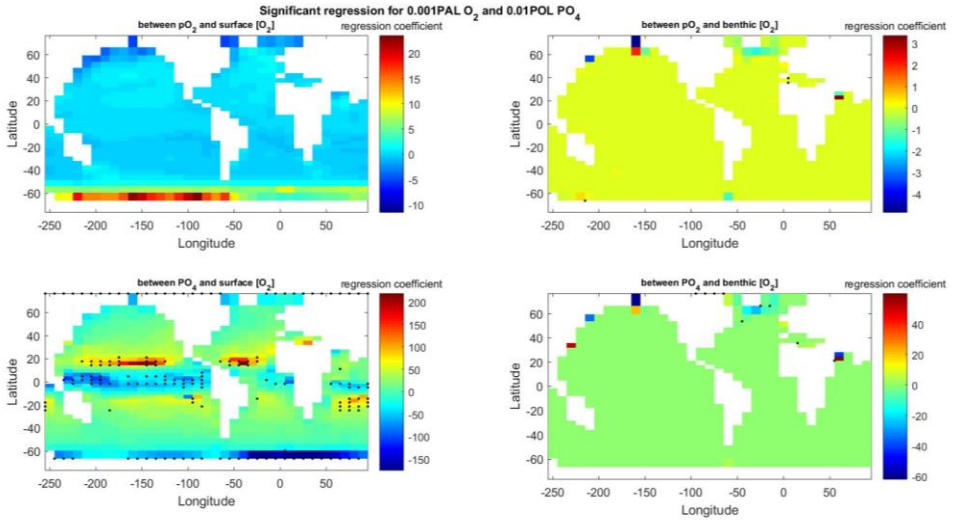
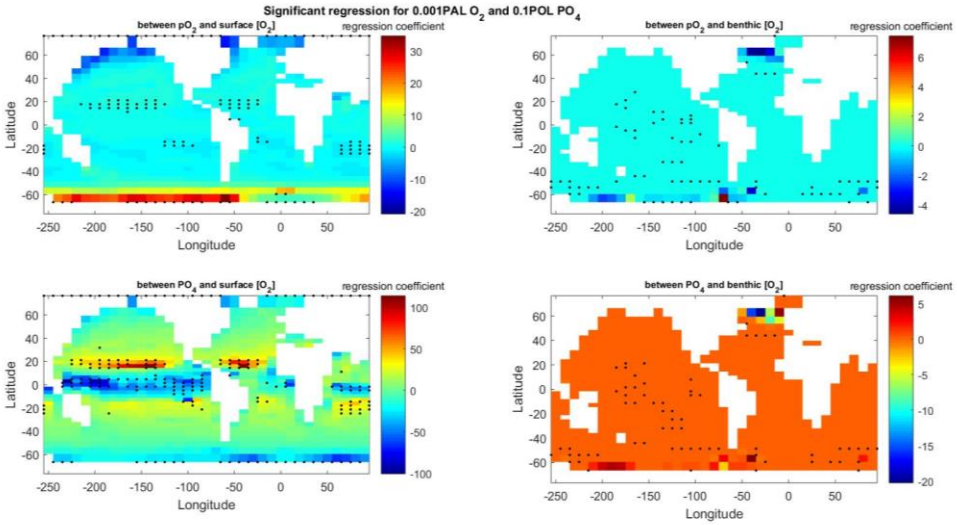
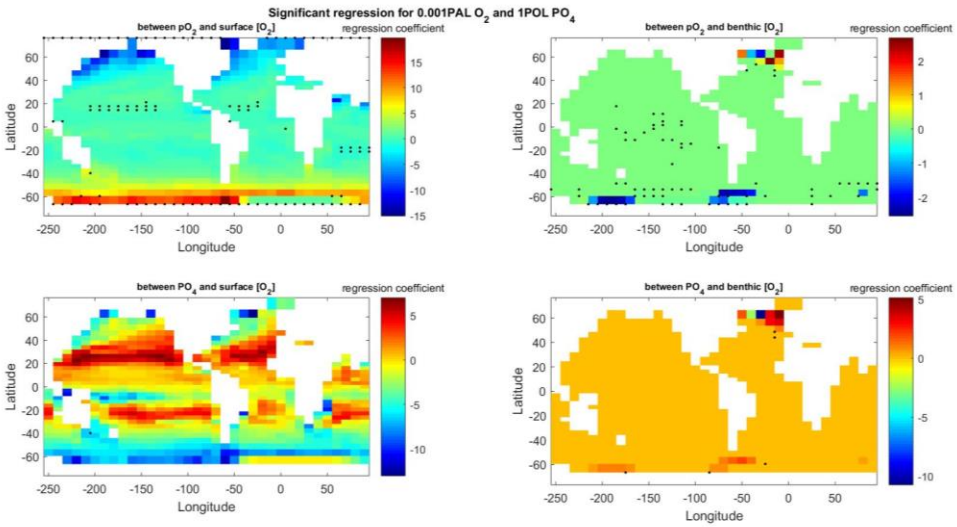
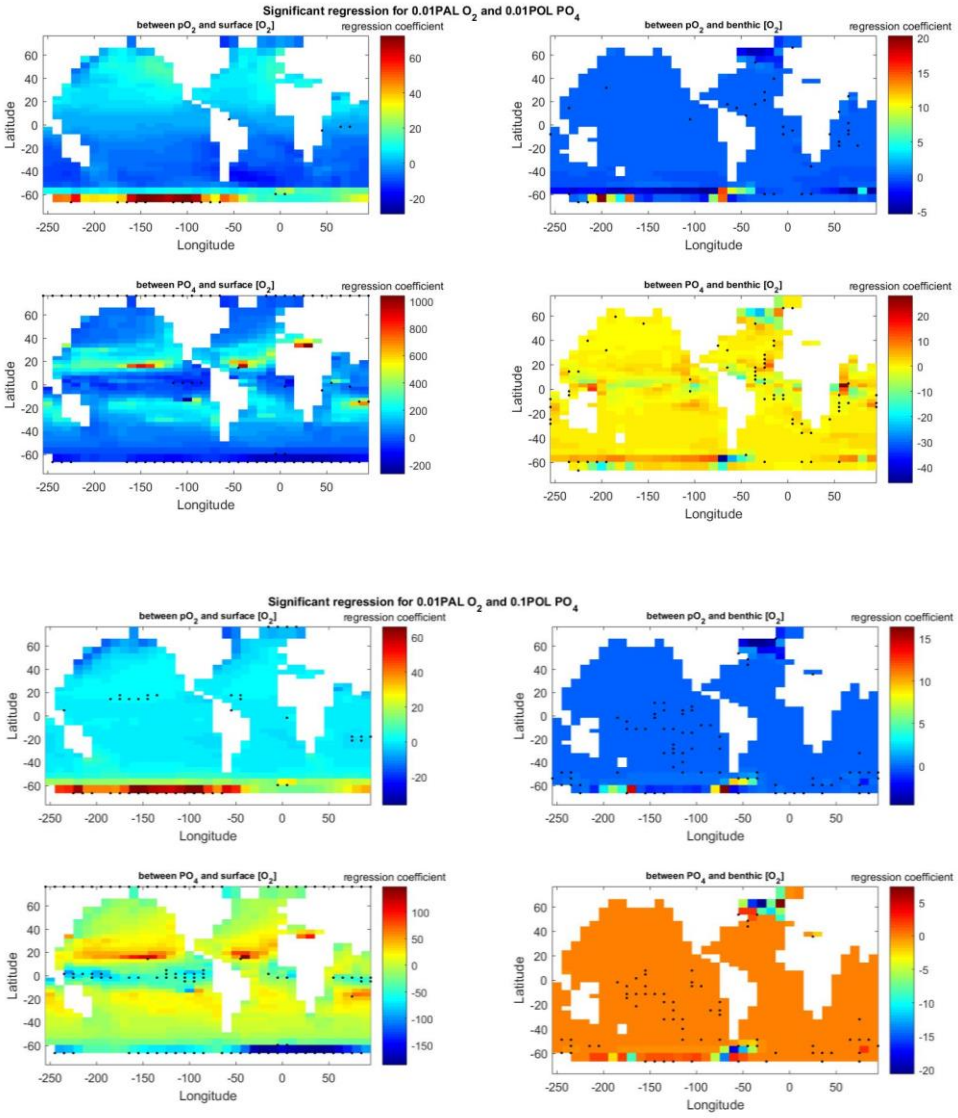


Figure S1. Distribution plots of surface ocean oxygen at other PO_4 levels


Significant regression for 0.001PAL O_2 and 0.01POL PO_4
between pO_2 and surface $[O_2]$
between pO_2 and benthic $[O_2]$
between PO_4 and surface $[O_2]$
between PO_4 and benthic $[O_2]$
regression coefficient
Latitude
Longitude


Significant regression for 0.001PAL O_2 and 0.1POL PO_4
between pO_2 and surface $[O_2]$
between pO_2 and benthic $[O_2]$
between PO_4 and surface $[O_2]$
between PO_4 and benthic $[O_2]$
regression coefficient
Latitude
Longitude


Significant regression for 0.001PAL O_2 and 1POL PO_4
between pO_2 and surface $[O_2]$
between pO_2 and benthic $[O_2]$
between PO_4 and surface $[O_2]$
between PO_4 and benthic $[O_2]$
regression coefficient
Latitude
Longitude


Significant regression for 0.01PAL O_2 and 0.01POL PO_4
between pO_2 and surface [O_2]
between pO_2 and benthic [O_2]
between PO_4 and surface [O_2]
between PO_4 and benthic [O_2]
regression coefficient
Latitude
Longitude
Significant regression for 0.01PAL O_2 and 0.1POL PO_4
between pO_2 and surface [O_2]
between pO_2 and benthic [O_2]
between PO_4 and surface [O_2]
between PO_4 and benthic [O_2]
regression coefficient
Latitude
Longitude

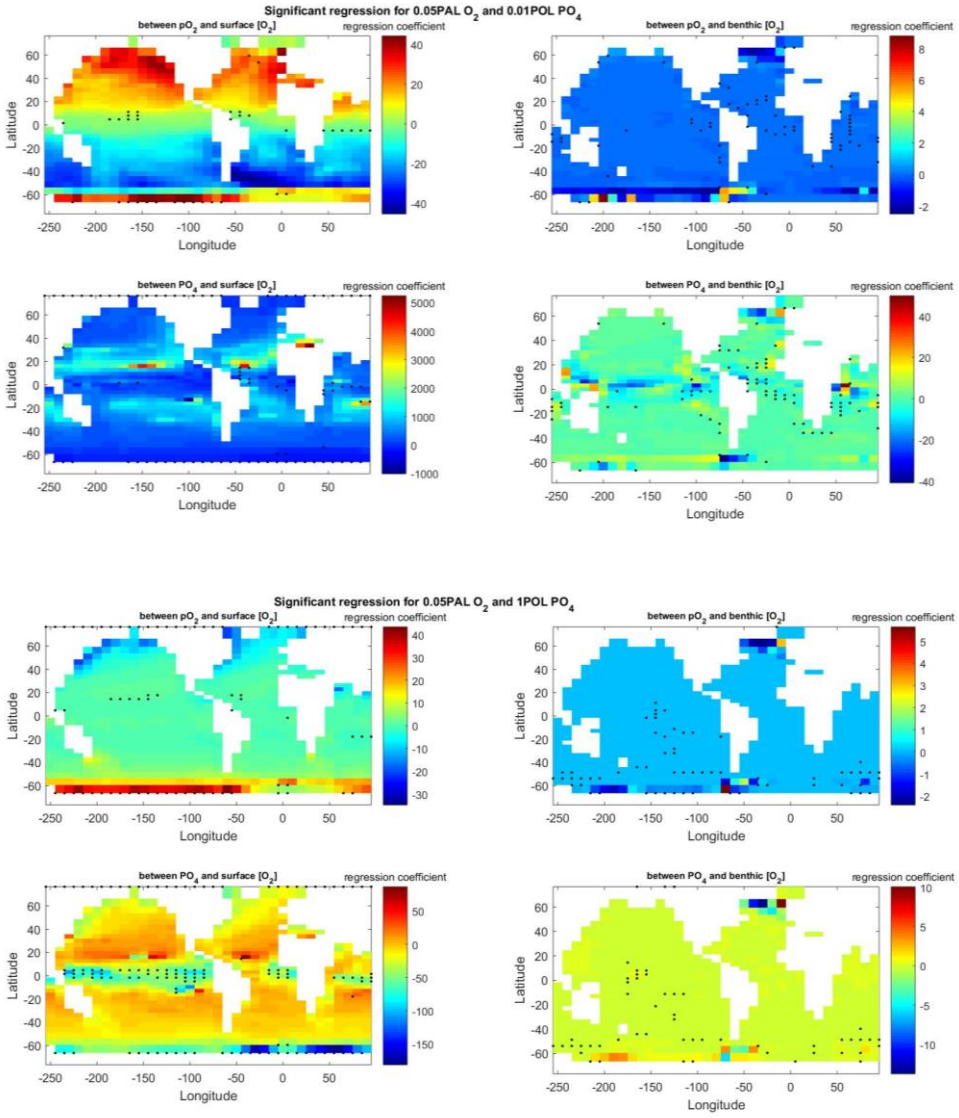


Figure S2. Other regression plots